

TITLE OF THE INVENTION

Mixed Conductor and Mixed Conductor Producing Method

BACKGROUND OF THE INVENTION

5 1. Field of the Invention

The present invention relates to a mixed conductor which exhibits both electronic~~ly~~ conduction and proton conduction. This mixed conductor can be used for the catalyst layer of a fuel cell, a gas diffusion catalyst and the like.

10 2. Description of the Related Art

The catalyst layer of a fuel cell is formed between a proton exchange membrane and a backing layer and supports a catalyst for accelerating an electrochemical reaction. ~~A combination of the catalyst layer and the catalyst layer~~ constitutes the electrodes of the fuel cell. In the catalyst
15 layer on an air cathode side, for example, protons passing through the proton exchange membrane and electrons transferred to the air cathode are conducted ~~up~~ to the catalyst, thus binding oxygen and protons diffused onto the catalyst. ~~Namely~~ ^{Thus}, the catalyst layer needs to exhibit both proton conduction and electronic~~ly~~ conduction in order to ~~improve~~ ^{reduce} the transfer loss of
20 oxygen, protons and electrons. To this end, a mixture of poly electrolyte having catalysts supported on surfaces such as carbon particles (exhibiting electronic~~ly~~ conduction) and Nafion (trade name, manufactured by E.I du Pont de Nemours, ~~this applies hereafter~~) which exhibits ionic conduction is used in the fuel cell.

25 However, if a material having ionic conduction and a material having electronic~~ly~~ conduction are used together, it is difficult to mix them ~~up~~ completely uniformly. As a result, protons and electrons cannot be

uniformly transferred to all catalyst particles.

To solve this disadvantage, there has been proposed a mixed conductor which exhibits both ionic conduction and electronic conduction using one material.

5 For example, organic mixed conductors are disclosed in the following patent documents 1 to 4.

In addition, inorganic mixed conductors conducting electrons and oxygen ions are disclosed in the following patent documents 5 to 8.

10 Patent Document 1: Japanese Unexamined Patent Publication No. 2001-202971

Patent Document 2: Japanese Unexamined Patent Publication No. 2001-110428

Patent Document 3: Japanese Unexamined Patent Publication No. 2003-68321

15 Patent Document 4: Japanese Patent Application National Publication (Laid-Open) No. 2002-536787

Patent Document 5: Japanese Unexamined Patent Publication No. (10)1998-255832

20 Patent Document 6: Japanese Unexamined Patent Publication No. (11)1999-335165

Patent Document 7: Japanese Unexamined Patent Publication No. 2000-251533

Patent Document 8: Japanese Unexamined Patent Publication No. 2000-18811

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Since the organic mixed conductors are made of organic materials, they have many problems in terms of durability and heat resistance to be

solved before being put to practical use.

As for the ~~Inorganic~~ mixed conductors which transfer electrons and oxygen ions, ^{have high} operating temperatures thereof are high (about 800°C). Due to this, it is considered that these inorganic mixed conductors are ^{and therefore} inappropriate for small-sized fuel cells suitably ^{e for} used in, for example, vehicles and cellular phones.

SUMMARY OF THE INVENTION

After exerting utmost efforts in study to solve these disadvantages, the inventor of the present invention discovered a novel inorganic mixed conductor and finally completed the present invention.

^{In order to solve the foregoing problems, provides} That is, the inventor of the present invention discovered a mixed conductor ^{in the form of} characterized in that an electron conductor made of an inorganic material ^{is} fixed to a proton conductor made of an inorganic material so as ^{to be insoluble} not to dissolve in water.

^{The inorganic may be} As the electron conductor made of an inorganic material, an electron conductor of such a type ^{with} as to cause a main chain ^{having} to have one or both of a carbon-carbon double bond and ^{or} a carbon-carbon triple bond, the main chain contributing to ^{the} an electronic conduction function as shown in Figs. 1 and 2. ^{Alternatively, the inorganic electron may be} may be used on such a type as to transfer electrons through a side chain.

^{The red which inorganic is} It is also preferable that such an electron conductor ^{at least one} uses an inorganic material obtained by carbonizing an organic compound having a π bond. Examples of ^{the} organic compound ^s having a π bond include aliphatic hydrocarbon^s, aromatic hydrocarbon^s and derivatives of ^{the} aliphatic hydrocarbon^s and ^s the aromatic hydrocarbon^s. ^{At least one of them is used} for the organic compound having the π bond. Typical examples of ^{such} the organic compounds include polyacetylene, resorcinol, phenol, phenylphenol,

polyaniline, polypyrrole, polythiophene, phenylphosphonic acid, and phenylsilane alkoxide.

Further, the inorganic ~~material for the~~ electron conductor can be a carbonaceous material, such as graphite or a carbon nanotube, or a metallic material containing a metal such as gold, palladium, platinum, magnesium, lithium or titanium, or an alloy thereof.

As the ^{inorganic} proton conductor ^{is} made of ~~an inorganic material~~, ^{at least} one of a phosphorus-containing compound, a sulfur-containing compound, carbonic acid, boric acid, and inorganic solid-state acid, ^{more preferably,} ^{particularly} at least one of a phosphorus-containing compound, phosphoric acid, phosphoric ^{acid} ester, sulfuric acid, sulfuric ^{acid} ester, sulfuric acid, tungsten oxide hydroxide, rhenium oxide hydroxide, silicon oxide, tin oxide, zirconia oxide, tungstophosphoric acid, and tungstosilicic acid, ~~can be used.~~

According to the present invention, the inorganic electron conductor and the inorganic proton conductor are fixed to each other so as ~~not~~ to ^{be} ~~dissolve~~ ^{insoluble} in water.

No π → They may be fixed by ~~a~~ ^{ing} covalent bond, intercalation or inclusion. However, depending on production process conditions, these ^{types} ~~manners~~ of fixing may ^{combined} possibly be ~~mixed~~.

20 Further, ~~whether the state of fixing is by~~ ^{choice of} covalent bonding, intercalation or inclusion is ^{made} set according to the types of the materials of the electron conductor and the proton conductor. For example, if the electron conductor is ~~made of~~ an inorganic material obtained by carbonizing an organic material, the fixing may be ~~made~~ ^{ing} mainly by a covalent bond. If the electron conductor is made of a metal ^{lic} material and an inorganic material, ^{especially} ~~particularly~~ an oxide is selected as ^{the} a material for the proton conductor, for example, the both conductors can be fixed to each other by ~~a~~ ^{ing} covalent bonding.

or inclusion.

The state in which the electron conductors and the proton conductors are fixed to each other by ^{ins} a covalent bond is illustrated in Figs. 1 and 2. Since the electron conductors 1 or 3 and the proton conductors 2 bound by ^{ins} a covalent bond are arranged in close proximity, both the electron conductors and the proton conductors can contact ~~with~~ a catalyst particle (e.g., platinum) in nano order as shown ~~therein~~. Accordingly, it is possible to supply electrons and protons necessary for a catalytic reaction to the catalyst in proper quantities.

10 Such a mixed conductor is formed as follows.

First, a precursor obtained by dispersing a proton conductor ~~into~~ a polymer of an organic compound having a π bond is prepared.

The precursor having a proton conductor dispersed ~~into~~ the polymer of an organic compound, or the precursor having both a proton conductor bound to an organic compound that constitutes the electron conductor by a covalent bond and a proton conductor separated from the former proton conductor and substantially in a dispersed state.

Further a high molecular ^{weight} precursor may be formed by polymerizing an organic compound having a π bond with a proton conducting material.
 20 ~~In this high polymer precursor, it is considered that the carbons mainly constituting the organic compound are polymerized with one another to form an electron conducting main chain having a π bond and also form a covalent bond with the proton conductor, and that this proton conductor bridges the carbon main chain of the electron conductor. By ~~mixing~~ ^{adding} the~~
 25 proton conductor in ^a sufficient quantity, the distance between the proton conductors bound to the carbon main chain by covalent bonds is narrowed, and proton conduction is generated between the proton conductors.

~~It has been experimentally shown that~~
 According to research by the inventor, putting the polymer precursor in ^{to} a solution ^{with} of hydrolytic cleavage at 100 to 200 °C for several hours promotes formation of ^s to form covalent bond between the electron conducting main chain and the proton conductor, ~~thereby~~ ^{ins} it causes improvement on proton conductivity and prevention ^{ins} for releasing ^{e of} the material of proton conductivity ^{or} from the polymer precursor. ^{subjected to}

This precursor is pyrolysis ⁱⁿ under an inert atmosphere. As a result, the organic compound is ^{converted} carbonized into an inorganic material, thereby ensuring electronic conduction.

10 ~~Because~~ In addition, the proton conductor is stably fixed to the electron conducting carbon skeletons. ~~As a result,~~ proton conduction is ensured. It is ^{believed} ~~considered~~ that the proton conduction is attained by arranging proton conductor ^s ~~allocation materials to be~~ proximate ~~to~~ each other. As shown in Figs. 1 and 2, if the proton conductors bridge the
 15 carbon skeletons, the positions of the proton conductors are fixed, thereby ensuring the proton conduction by the interaction between the proton conductors.

If the proton conductors are released from the carbon skeletons or if the proton conductors are not bound to the carbon skeletons from the ~~state~~
 20 ~~of the precursor, then it is considered that the proton conductors are~~ ^{believed} to be intercalated into the carbon main chain or included in a mesh structure formed by the carbon main chain. In any case, ~~it is considered that~~ the proton conduction can be ensured ^{provided} ~~as long as~~ the proton conductors are in ^{close} proximity.

25 ~~As can be seen,~~ Since the proton conductors are bound, intercalated or included between the carbon skeletons, the proton conductor does not float. ^{Therefore,} ~~Due to this,~~ even if the mixed conductor is used at a location where

water is present, the proton conductor ^{is influenced} does not flow out by the water. That is, ^{the loss of} a rate of lowering the proton conduction ^{in the presence of} by water is very low.

Now, ~~examples of the~~ Organic compounds having a π bond include unsaturated aliphatic hydrocarbons and aromatic hydrocarbons. More ^{preferably} ~~concretely~~, at least one of polyacetylene, resorcinol, phenol, phenylphenol, polyaniline, polypyrrole, polythiophene, phenylphosphonic acid, and phenylsilane alkoxide ^{is} ~~can be~~ selected as a material for the organic compound having a π bond.

Further, ~~examples of the~~ proton conducting material include ~~a~~ phosphorus-containing compound, ~~a~~ sulfur-containing compound, carbonic acid, boric acid, and inorganic solid-state acid. ^{An} ~~Examples~~ of the phosphorus-containing compound ^{is} ~~include~~ phosphoric acid and ~~principle~~ examples of the sulfur-containing compound include sulfuric acid and sulfonic acid. Further, an inorganic proton conducting material can be produced using a derivative of one of these compounds as a starting material. ^{Preferably,} ~~In this case, particularly~~ at least one of a phosphorus-containing compound, phosphoric acid, ester phosphate, sulfuric acid, ester sulfate, ~~sulfuric acid~~, tungsten oxide hydroxide, rhenium oxide hydroxide, silicon oxide, tin oxide, zirconia oxide, tungstophosphoric acid, and tungstosilicic acid ^{is} ~~can be~~ used.

To mineralize the organic compound in the precursor, it is preferable that the precursor ^{be pyrolyzed in} ~~is burned under~~ an inert atmosphere.

The inert atmosphere can be attained by putting the precursor ^{in an atmosphere} ~~under the distribution~~ of nitrogen gas or helium gas or in vacuum.

If the precursor is ^{subjected to} ~~pyrolysis under~~ ⁱⁿ such an inert atmosphere, the organic component of the precursor is carbonized ^{and thereby converted} into an inorganic material. If the main chain of the organic component has a π bond, high electron

conduction is ensured.

Heating temperature and heating time are appropriately selected according to the characteristics of the precursor.

Simultaneously with or after heating, ~~high energy~~ ^{radiation} ~~other than heat~~ ^{radiation} can be applied to the precursor. Examples of the high energy include plasma radiation, microwave radiation and ultrasonic radiation.

As described above, the mixed conductor according to the present invention is made of inorganic materials and exhibit both an electron conducting function and a proton conducting function. In addition, even in a low temperature range close to ~~room~~ ⁵ room temperature, the mixed conductor functions properly. Further, even if water is present, the mixed conductor exhibits both electron conduction and proton conduction.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a ~~typical view~~ ^{schematic representation of} illustrating the structure of a mixed conductor according to the present invention;

Fig. 2 is a ~~typical view~~ ^{schematic representation of} illustrating the structure of ~~the~~ ^{another} mixed conductor according to the present invention;

Fig. 3 is a ~~typical view~~ ^{schematic representation of} illustrating the structure of ~~the~~ ^{yet another} mixed conductor ~~in one embodiment~~ according to the present invention;

Fig. 4 is a ~~typical view~~ ^{schematic} of a ~~holder~~ ^{element} for checking the proton conducting function of the mixed conductor ~~in the embodiment~~ ^{of invention};

Fig. 5 is a chart showing the current-voltage characteristics of the ~~holder~~ ^{element} shown in Fig. 4; and

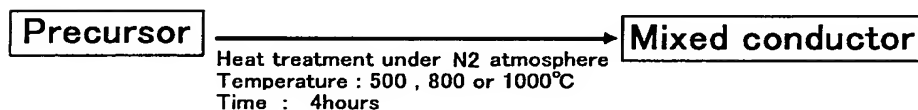
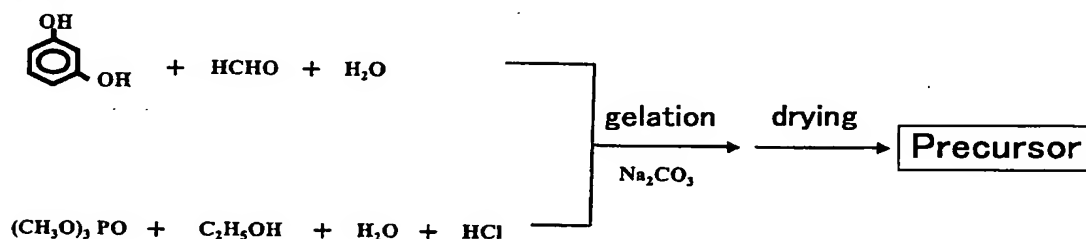
Fig. 6 is a chart showing the change ⁱⁿ of a phosphoric acid ~~remaining~~ ^{content} ~~rate~~ ^{immersed} with time in the mixed conductor in pure water ~~in the embodiment~~.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The above-stated advantages of the mixed conductor according to the present invention ~~will be confirmed hereinafter by way of exemplary embodiments.~~ *are by the examples which follow.*

First, a method for producing a mixed conductor will be described with reference to the following chemical formula 1 as well as Fig. 3.

Chemical formula 1



Resorcinol (10 g) and formaldehyde (13 ml) are dissolved in water (40 ml), and a solution obtained by hydrolyzing trimethyl phosphate is added ~~to the solution~~. *then* The solution is subjected to reflux at 100 to 200°C for four hours and covalent bond *ing* between electron conductor and proton conductor in the solution is promoted. The resultant solution is dehydrated and condensed with ~~Na₂CO₃~~ *Na₂CO₃* as a catalyst to gelate the solution. This gel is dried at 120°C, thereby obtaining a precursor.

This precursor is subjected to ~~pyrolysis~~ *pyrolysis* (at 500 to 1000°C) under a

nitrogen atmosphere to obtain a mixed conductor ^{wherein} ~~in the embodiment.~~ This ~~mixed conductor is constituted so that~~ electronic conductor phases 7 of a graphite-like structure and ^a proton conductor phase 9 containing phosphoric acid group^s are alternately aligned as shown in Fig. 3.

- 5 The mixed conductor thus obtained is ground, pressed ^{placed} ~~into~~ a plate, and ^{and supplied with} ~~put~~ between current collecting plates to supply a DC current, ~~to the plate-formed mixed conductor.~~ Specific resistance of each embodiment is obtained from a voltage at ~~that time.~~ ~~Measurement temperature is a room temperature.~~

10

	Example Embodiment 1	Example Embodiment 2	Example Embodiment 3
Heat treatment temperature	500°C	800°C	1000°C
Specific resistance (Ω cm)	138	0.35	0.13

- ~~The reason for~~ ^{The} ~~in the embodiments, the reason of~~ high specific resistance ^{for the sample heat treatment} at a ^{due to} heating temperature of 500°C is considered to be insufficient carbonization ^{the} of an organic material.
- 15

The heating temperature and heating time are parameters that can be appropriately selected according to the structure and the like of the organic compound.

- 20 Next, a proton conduction test will be described with reference to Figs. 4 and 5.

As shown in Fig. 4, a backing layer 17 consisting of a carbon cloth and catalyst layer 15 is attached to each side of a sample 11 in each of ^{Examples} ~~Embodiments~~ 1 to 3. A Nafion membrane 13 transmits protons but blocks

electrons.

A holder shown in Fig. 4 is put in a container, and nitrogen gas or hydrogen gas at a temperature of 60°C and a relative humidity of 100% is introduced into the container. ^{The} A voltage-current characteristic at that time

5 is shown in Fig. 5.

As can be seen from Fig. 5, even if a voltage is supplied between the backing layers 17 while introducing the nitrogen gas, no current is carried. On the other hand, if hydrogen gas is introduced into the container, it can be seen that a current flows. This demonstrates that the sample 11 has
10 proton conduction.

Further, the proton conductivity of each sample is calculated as follows.

	<i>Example</i> Embodiment 1	<i>Example</i> Embodiment 2	<i>Example</i> Embodiment 3
Heat treatment temperature	500°C	800°C	1000°C
Proton conductivity (S/cm)	2.6×10^{-3}	1.3×10^{-3}	7.3×10^{-4}

15 Further, as comparative examples, the proton conductivities of samples similarly subjected to a heat treatment by the ~~formation method in~~ ^{but with omission of addition of} ~~the embodiments already described above and to which trimethyl phosphate,~~ ^{were} ~~are not added~~ are calculated as follows.

	Comparative Example 1	Comparative Example 2	Comparative Example 3
Heat treatment temperature	500°C	800°C	1000°C
Proton conductivity (S/cm)	1.0×10^{-6} or less	1.0×10^{-6} or less	1.0×10^{-6} or less

A comparison of

By comparing the samples to which trimethyl phosphate ^{was} added with those to which trimethyl phosphate ^{was} not added, ^{confirms the} ~~the appearance of~~ proton conduction by phosphorus ~~is proven.~~

- 5 The relationship between immersion time and ^{remaining} phosphorus ^{content} ~~remaining rate~~ when samples (0.1 g) ^{of} ~~in~~ the respective ^{examples} ~~embodiments~~ are immersed in 1000 cc of pure water at a room temperature is shown in Fig. 6.

In Fig. 6, the phosphorus ^{residual amount was} ~~remaining rate is~~ measured by an EDX analyzer.

- 10 The result shown in Fig. 6 confirms that about 60% of phosphorus, about 80% of phosphorus, and about 90% of phosphorus (i.e., proton conduction) remains in the samples ^{of examples} ~~in Embodiments~~ 1, 2, and 3, respectively, ^{which}

- ^{as invention} ~~This~~ demonstrates that the mixed conductors ~~in the embodiments~~ ^{retain} keep their proton conducting functions even in a humid environment for a long time.

- The mixed conductors can be used for fuel cells, and ^{it} particularly suitably ^{e for} ~~used for~~ as the catalyst layers ^{of} ~~constituting the respective~~ fuel cells. The catalyst layer is a location where oxygen or hydrogen supplied from the outside through the backing layers is ionized, and is normally arranged between the proton exchange membrane and the backing layer.
- 20

Examples of a method for producing a catalyst layer ~~if one~~ of the mixed conductors ~~is used as the catalyst layer~~ will next be described.

Working Example 1

(Example 1)

- 25 Each of the mixed conductors produced above is ground to powder by a ball mill or the like, and ^{a platinum catalyst is supported on} ~~the mixed conductor thus ground is caused to~~ support a platinum catalyst. ^{platinum catalyst} ~~The mixed conductor can be made to supported on the~~

~~the platinum catalyst~~ by the same method as ^{used to form} ~~that for causing a carbon~~
~~holder in a process of forming a supported platinum~~ ^{catalyst used as} ~~carbon that constitutes~~
 the catalyst layer of an ordinary fuel cell, ~~to support a platinum catalyst.~~

For example, chloroplatinic acid solution is impregnated with the mixed
 5 conductor powder and then subjected to a reducing treatment, ^{thereby forming} whereby the
 mixed conductor ~~can~~ ^{ed} support platinum catalyst.

The supporting mixed conductor is ^{added to} ~~mixed into~~ a Nafion solution, ^{and mixed to produce} a
 paste of ~~a mixture thereof is produced~~ ^{the}, and this paste is screen-printed on
 each surface of an proton exchange membrane (a Nafion membrane in this
 10 example). As a result, a catalyst layer containing the mixed conductor is
 formed. Further, a backing layer is ^{attached} ~~connected~~ to the outside of the catalyst
 layer, whereby a unit fuel cell ^{of a} ~~that constitutes the fuel cell~~, i.e., a unit cell,
^{is} ~~can be~~ produced.

^{Working}
 Example 2

15 Each of the mixed conductors produced above is ground to powder by
 a ball mill or the like, and ^{is supported on} the mixed conductor thus ground, ~~is caused to~~
~~support~~ a platinum catalyst.

Next, the powder of the mixed conductor which supports the catalyst
 is subjected to hot pressing, thereby forming the mixed conductor into a
 20 shape corresponding to a target electrode to produce a catalyst layer. This
 catalyst layer is superposed on the proton exchange membrane and ^{the whole is} hot
 press ^{ed} ~~is conducted~~, whereby an integral ^{structure} ~~formed~~ article having the proton
 exchange membrane ~~put~~ between the catalyst layers is produced.

By ^{attaching} ~~further connecting~~ a backing layer to the outside of the catalyst
 25 layer, a unit cell of the fuel cell ^{is} ~~can be~~ produced.

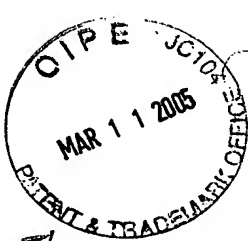
In the tests ^{described} ~~stated~~ above, the mixed conductors ^{as} ~~in~~ the examples
 exhibit both proton conduction and electronic ~~conduction~~ at a low

temperature, in a range of ^{from} a room temperature to 60°C. Depending on the presence of water, it is ~~considered that~~ the mixed conductors exhibit ~~the~~ equivalent functions up to 200°C ^{in the} ~~under an~~ atmosphere.

It is seen that the mixed conductors ^{as the present invention} ~~in the embodiments can~~ exhibit
 5 their functions even at an extremely low temperature as compared with the conventional inorganic-based mixed conductor which exhibits its functions at a high temperature of about 800°C.

Furthermore, as is obvious from the structure shown in Fig.3, the electronic conductor phase 7 is connected to the proton conductor phase 9 by
 10 a covalent bond, so that they are quite proximate to each other. Due to this, even if a catalyst particle is very small, the electron conductor 7 and the proton conductor 9 can ^(be always) brought into contact with the catalyst particles simultaneously. This makes it possible to supply electrons and protons necessary for a catalytic reaction to the catalyst in proper quantities
 15 and thereby improve ^S catalyst utilization efficiency.

The present invention is not limited ^{by} ~~at all by the embodiments and~~ ^{above} the description of the embodiments. The present invention also ^{includes} ~~contains~~ various changes and modifications thereto without departure from the description of claims which follow in a range that can be easily attained by a
 20 person having ^{the level of} ordinary skill in the art.



ABSTRACT OF DISCLOSURE

~~The~~ mixed conductor of ~~this~~ ^{the} invention includes an electron conductor made of a carbon-based inorganic material ^{with} ~~imparted~~ ^{ing} ~~electron conduction by causing~~ ^{for conduction of electron} a main chain to have a π bond, and a proton conductor made of an inorganic material ~~having~~ ^{wherein} ~~proton~~ ^{attached} ~~conduction, and~~ the electron conductor and the proton conductor are fixed to each other by ~~one of or all~~ ^{at least one} of a covalent bond, ^{ing} ~~intercalation~~, and inclusion.